

A. Project Summary

This proposal describes the use of a transportable aerosol time-of-flight mass spectrometer (ATOFMS) for continuous single particle analysis during the ACE-Asia Intensive Field Operations (ACE-Asia IFO). These real-time measurements will provide information on the aerodynamic size and chemical composition of individual particles detected in the area under study with high temporal resolution (i.e. 10-60 minutes depending on ambient particle concentration). ATOFMS measures the aerodynamic size of particles from a polydisperse sample with high precision. This precision allows for scaling ATOFMS data into atmospherically representative size-resolved chemical composition distributions with a high level of confidence. Information at this unique level will help address many of the principal scientific issues stated for the ACE-Asia Project, including determination of physical and chemical properties of aerosol particles, quantification of physical and chemical processes controlling their evolution, and assessment of the role of chemical composition of aerosol particles in climate change.

The proposed measurements will be carried out on the designated US Research Vessel because this will allow sampling of regional aerosol features at different locations and distances from continental influences. Of particular interest will be to assess the degree of mixing and reaction/aging of the particles present in the sampling locations in order to evaluate their temporal and chemical variability. The influence of these chemical changes on the radiative properties of the particles will then be characterized upon comparison of ATOFMS single particle data with radiometric measurements made simultaneously. Performing these comparisons that take into consideration chemical information at a single particle level will assist in establishing the important particle characteristics that influence climate change. ATOFMS data will be scaled to atmospherically relevant concentrations using data from co-located particle sizing (i.e. OPC, SMPS) and mass measurement instruments. The associated chemical speciation within individual particles as a function of size will be used to help refine current atmospheric chemistry models. Also, complementary laboratory studies will be conducted in order to further investigate heterogeneous reactions involving the observed aerosol, allowing for better interpretation of the results from this campaign. Variability in aerosol chemical composition due to gas-particles reactions is of great importance when trying to determine the influence of anthropogenic activities on the local and global environment.

The proposed ATOFMS single particle analysis will help identify and allocate relative contributions from different sources, using distinct combinations of ion markers from the single particle mass spectra. Differences in the size-resolved chemical composition distributions as a function of time of day, weather conditions and air mass trajectories will be used to help understand the variability in aerosol particles observed during various periods of the study.

The success of international multidisciplinary programs designed to address the uncertainties in global climate change, such as ACE-Asia, will help in the development of a better understanding of the impact of anthropogenic pollution (with consequent influences in regulatory, scientific, and social environments).

C. PROJECT DESCRIPTION

Shipboard Measurements of Size-Resolved Single Particle Chemistry with a Transportable Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) during the 2001 ACE-Asia Intensive Field Operations

C.1. Results from Prior NSF Support

Grant ATM9612887 (“Indian Ocean Experiment”) represents the NSF project most closely related to the proposed ACE-Asia project (July 1, 1998 to June 30, 1999). This funding (\$200,000, no overhead) was provided by NSF via the Center for Clouds, Chemistry, and Climate (C4) at the Scripps Institute for which Professor Prather became a PI as part of this project. This funding supported two graduate students in the Prather group to operate an ATOFMS instrument in the Indian Ocean experiment (INDOEX). Details for the results from this study are provided below. The presented results demonstrate the type of data collection and analysis we propose to perform during ACE-Asia.

During the Indian Ocean Experiment-Intensive Field Phase 99 (INDOEX-IFP 99), ATOFMS single particle data were collected on the Island of Kaashidhoo (4.965°N, 73.466°E) in the Republic of Maldives, as well as during cruise Legs #2 and #3 on the NOAA R/V Ronald H. Brown (see Figure 5) during February and March of 1999. ATOFMS data (a total of 18 GB of single particle mass spectra) provide unique information on the temporal variations of the aerosol chemical composition in the studied regions during INDOEX. The data are being used to evaluate the role of the aerosol particle chemistry on global radiative forcing, visibility, and other physical properties of the atmospheric aerosol during this study.

The ATOFMS instrument operated continuously 24 hours a day for a total of fifty-four days during the INDOEX-IFP 99. Particles in the 0.2 to 3.0 μm aerodynamic diameter size range were classified in different classes according to the mass spectral information obtained. A distinct break at 1 μm existed in the types of particles detected during the study. Below 1 μm , the particles were composed primarily of organic species and/or elemental carbon. In contrast,

above 1.0 μm , particles were classified mostly as dust and sea salt. Positive and negative ion mass spectra of individual particles were then used to further classify the particles to assess degrees of association of different species.

In Figure 1, representative laser desorption/ionization (LDI) mass spectra of a single particle classified as sea salt with nss (non sea salt) sulfates are presented as an example. The main features of the positive ion mass spectrum for sea salt particles are the presence of peaks at m/z 23, 46, 62, 63, 81 and 83, that can be assigned to Na^+ ,

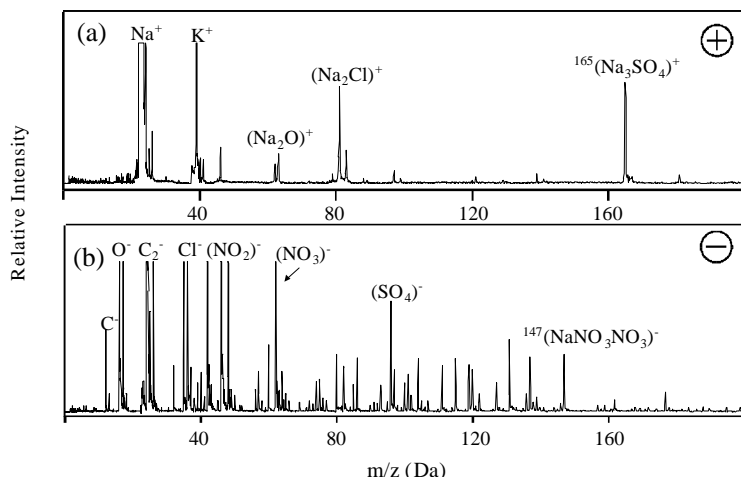


Figure 1: Positive (a) and negative (b) ion mass spectra of an individual sea salt particle with nss (non sea salt) sulfate.

Na_2^+ , NaO^+ , Na_2OH^+ , $\text{Na}_2^{35}\text{Cl}^+$ and $\text{Na}_2^{37}\text{Cl}^+$ respectively. The peak at m/z 165 (Na_3SO_4^+) typically indicates the presence of nss sulfates in this particle type. Also peaks that correspond

to Ca^+ and K^+ occur at m/z 40 and 39 and 41, respectively. The most noticeable features in the negative ion mass spectrum of sea salt particles are peaks at m/z -46, -62, -16, -17, -35 and -37 that can be assigned to NO_2^- , NO_3^- , O^- , OH^- , $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ ions respectively.

At certain times additional peaks appear in the particle mass spectra allowing further refinement of the particle classes. For example, differences in composition from particles classified as sea salt permit this class to be subdivided into eight categories: a) unreacted sea salt particles, b) reacted sea salt particles with nitrates, c) sea salt particles with organic matter, d) reacted sea salt particles with nss (non sea salt) sulfates, e) sea salt particles with organic matter and nitrates, f) sea salt particles with organic matter and nss sulfates g) sea salt particles with nitrates and nss sulfates, h) sea salt particles with organic matter, nitrates and nss sulfates.

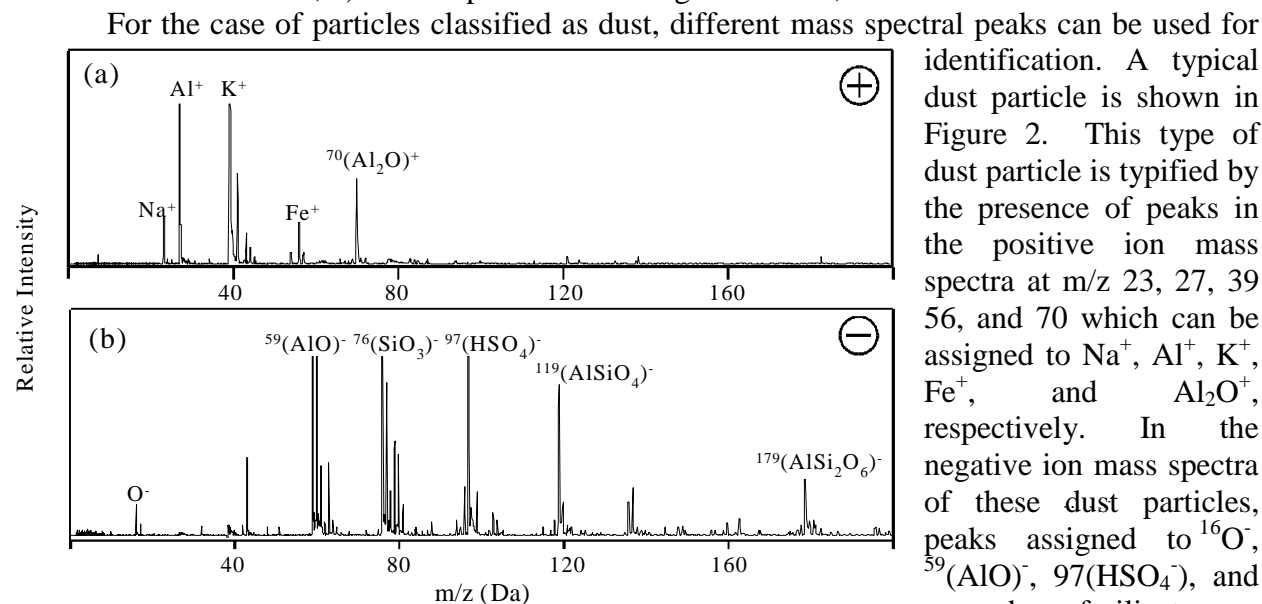


Figure 2: Positive (a) and negative (b) ion mass spectra of a typical dust particle detected over the Indian Ocean.

were a number of other dust particle types detected during INDOEX. Another common type showed peaks in the positive ion mass spectra at m/z 48, 64, 82, and 99 Da that can be assigned to Ti^+ , $^{64}(\text{TiO})^+$, $^{82}(\text{TiO}_2\text{H}_2)^+$ and $^{99}(\text{TiO}_3\text{H}_3)^+$. For the case of sulfates associated with dust particles, the relevant sulfate marker in the negative ion mass spectra is $^{97}(\text{HSO}_4)^-$ or $^{96}(\text{SO}_4)^-$. Further refinement of the chemical classes for dust particles is also possible by using additional indicative ion peaks in the mass spectra (e.g. presence of nitrates, organics, etc) as described for sea salt particles.

As mentioned above, particles with aerodynamic diameter smaller than $1.0\ \mu\text{m}$ were mostly classified as carbon containing and/or elemental carbon. This observation is consistent with previous ambient studies using ATOFMS (Noble and Prather 1996). Ions commonly observed in the mass spectra of particles classified as carbon containing are described in Section C.4 (Rationale and Significance).

After classifying the particles into different classes, the chemical composition of the observed aerosol can be inferred as the percentages of particles classified into each of the exclusive categories. The number of particles of each class detected with the ATOFMS is corrected for transmission efficiency prior to the determination of relative percentages. In order

to account for the ATOFMS transmission efficiency, an optical particle counter (OPC) was used alongside the ATOFMS at all times in both platforms. Also, available number distribution data from instruments (i.e. scanning mobility particle sizer (SMPS)) belonging to other groups can be used to further corroborate the scaling.

In Figure 3, an example of the data collected during the intensive field period shows the aerosol chemical composition observed on March 27, 1999 (from 06:10 to 17:44 UT) on board of the NOAA R/V Ronald H. Brown (moving from 2.56°N 78.15°E to 2.31°N 80.35°E). For this figure, particles were classified into nine exclusive categories (from the mass spectra), and the contributions from each of these particle classes were evaluated with 0.1 μm resolution. It is important to note that these particles can be classified into even more refined categories (i.e. organic containing), however for clarity only nine classes are presented here. The sampled air mass during this period was determined to have a trajectory from India and/or Pakistan and the Arabian Sea. As shown in the figure, the major contributions for particles with aerodynamic diameter larger than 1.0 μm were from particles classified as sea salt, sea salt with nss sulfates, dust and dust with sulfates. For particles with aerodynamic diameter between 0.2 and 1.0 μm , the major contributions to the aerosol chemical composition were from particles classified as carbon containing with potassium and elemental carbon. When compared with the average aerosol chemical composition observed on the Island of Kaashidhoo (4.965°N, 73.466°E) during the month of February, where the observed air mass was usually determined to have an influence from the Bay of Bengal, a greater contribution from particles classified as sea salt with nss sulfates was found on March 27. This increase in the contribution of these particles could be an indication of an air mass that probably had existed over land for longer time periods, therefore allowing more time for reactions to take place. Also, this could be the result of an increase in sulfur components present in the atmosphere, or both. Also for March 27, an increased contribution from particles classified as dust and dust with sulfates was observed when compared with the average aerosol chemical composition observed at Kaashidhoo. This increased dust contribution was generally sustained when the sampled air mass had a trajectory linked with the Arabian Sea, India and/or Pakistan, indicating that the sampled air mass had spent more time over land. For the March 27 time period, particle number concentrations were approximately 2.3 cm^{-3} for particles with diameter between 1.0 and 2.5 μm and 63 cm^{-3} for those with diameter between 0.2 and 1.0 μm . Graphs such as the one presented in Figure 3 were derived on-site for each day of the IFP, allowing observation of variations in the chemical characteristics of the air masses being sampled and direct comparisons with other measurements.

Since the data obtained with the ATOFMS were stored in the Access database, further processing of the data at levels that allow for further comparison and interpretation can be easily performed. For example, this allows for further refinement of the chemical classification of the particles, changes in temporal and size resolutions, as well as searches for any chemical species of interest detected with the ATOFMS.

Data from the transportable ATOFMS during the INDOEX-IFP 99 have been compared with those obtained with collocated instruments from other research groups. Of special relevance is the comparison between ATOFMS and MOUDI impactor data (operated by Glen Cass's group from Caltech) obtained on the Island of Kaashidhoo. The ATOFMS data has been scaled (to account for transmission efficiency as mentioned above) and the resulting number distributions were converted to mass distributions (by using estimated particle densities) to compare mass distribution measurements from both instruments as previously described (Allen, Fergenson et al. 2000).

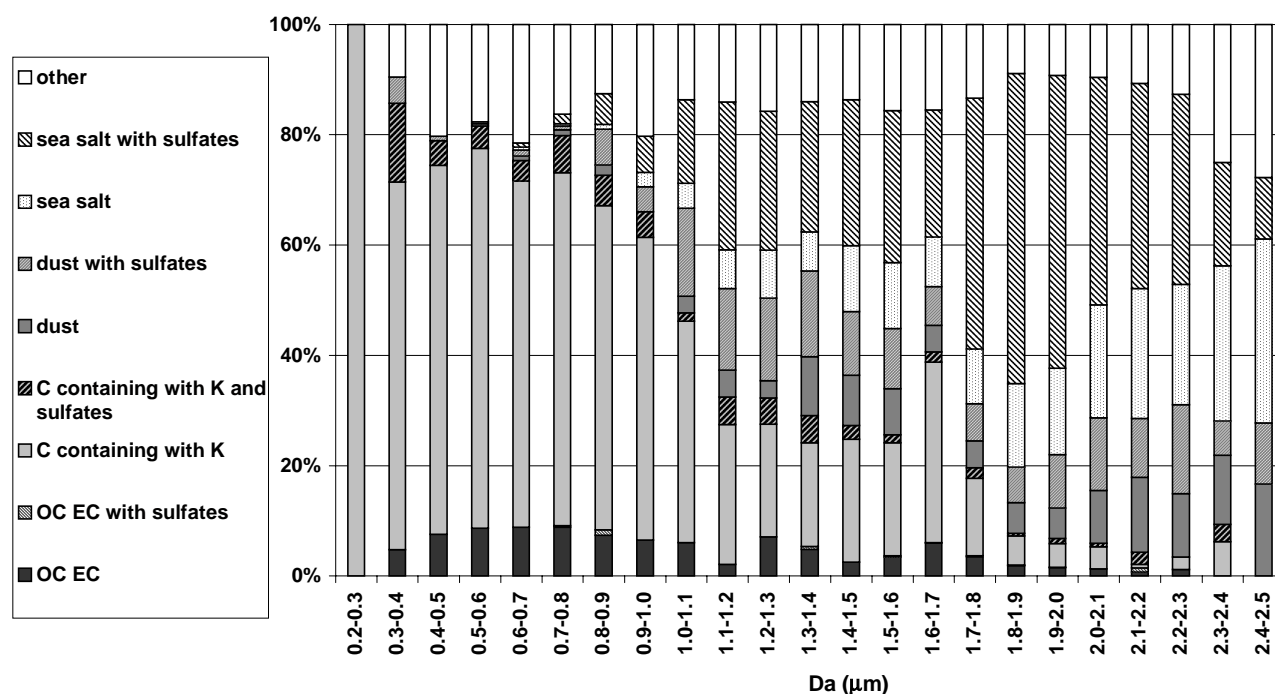


Figure 3: Evaluated aerosol chemical composition from ATOFMS single particle analysis (March 27, 1999). Particles were classified in nine exclusive categories from the mass spectra information obtained.

Further comparisons are being made, in particular those related to comparisons between gas-phase measurements and ATOFMS single particle measurements. An example of such comparison is the existence of good agreement between the measured gas-phase acetonitrile concentrations (determined by proton transfer reaction mass spectrometry PTR-MS operated by University of Innsbruck) and the number concentration of carbon containing particles with potassium detected by the ATOFMS. Acetonitrile is used as an indicator for biomass burning, and the combination of carbon-containing particles with potassium arises from different combustion sources, mostly biomass burning. The observed trends are consistent with measured CO and methanol concentrations over the same time period. The temporal evolution of carbon containing particles with potassium with aerodynamic diameters between 0.3 and 0.4 μm is shown in Figure 4 (from March 04 to March 22, 1999). These data were acquired on the R/V Brown while traveling on Leg #2 (shown in Figure 4). In this figure, the resulting particle number concentration for these particles is shown over time (UT) for 17 days with 10-minute temporal resolution. The main trends that are evident in the number concentration of these particles are consistent with those measured for acetonitrile concentrations as mentioned above. As shown in Figure 4, the number concentration for carbon containing particles with potassium is at a minimum during March 19, 1999, which corresponds to the southernmost location during Leg#2.

Also, integration of ATOFMS data with LIDAR and radiometric measurements is being carried out, allowing exploration of the exact extent to which aerosol composition can be linked with radiative forcing. An example of this type of integration is being made in order to correlate

diurnal changes in observed aerosol optical depth with changes in aerosol chemical composition as determined by ATOFMS single particle analysis.

These comparisons will allow determination of importance of different particle classes (as well as aggregations) on aerosol optical depth and radiative forcing.

All the results obtained during INDOEX-IFP 99 show the potential of ATOFMS single particle analysis for providing quantitative real-time information on different particle species of interest (such as carbon, sulfates, nitrates, etc.). Also, these results show the ability of ATOFMS single particle analysis to provide information on the state of aggregation and/or association of the particles, providing unique insight into the degree of internal and external mixtures of particles that can now be used to further refine atmospheric models. We propose to make similar measurements during ACE-Asia as described in the following sections.

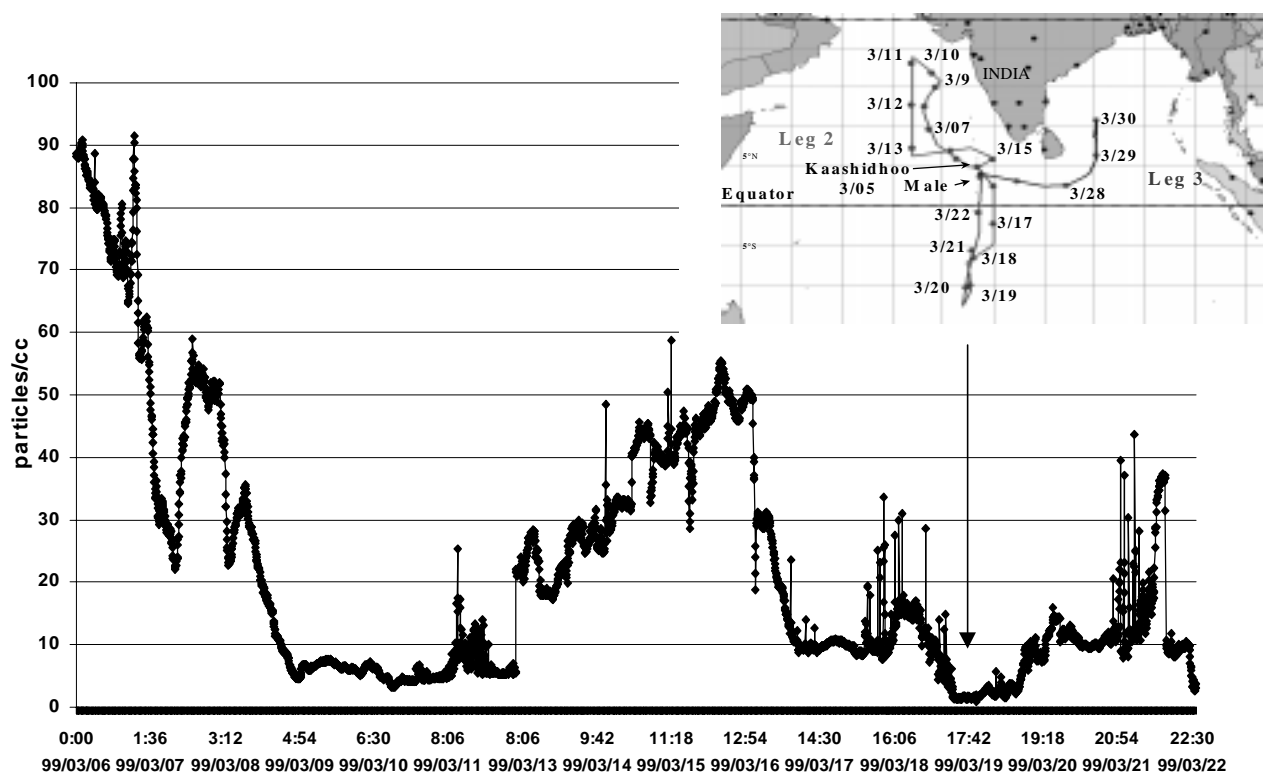


Figure 4: Temporal evolution of carbon containing particles with potassium (aerodynamic diameter between 0.3 and 0.4 μm) during Leg#2 on board NOAA R/V Ronald H. Brown. Insert shows the corresponding cruise trajectory.

C.2. Introduction

The importance of atmospheric aerosol particles, and sulfate aerosols in particular, in forcing climate change has been an emphasis of a number of studies in the past decade (e.g. Hoppel, Fitzgerald et al. 1990; Kiehl and Briegleb 1993; Huebert, Zhuang et al. 1996; Andreae and Crutzen 1997; Satheesh and Moorthy 1997; Bates, Huebert et al. 1998; Bates, Kapustin et al. 1998; Moorthy, Satheesh et al. 1998; Murphy, Anderson et al. 1998; Murphy, Thomson et al. 1998; Satheesh, Moorthy et al. 1998; Satheesh, Ramanathan et al. 1999). At present, tropospheric aerosols pose one of the largest uncertainties in model calculations of climate forcing due in large part to changes in the composition of the atmosphere brought about by anthropogenic activities (Intergovernmental Panel On Climate 1996; Hansen, Sato et al. 1998). The direct effect of aerosols relates to their ability to scatter solar radiation back into space, consequently reducing absorption and increasing the planetary albedo (Seinfeld and Pandis 1998). The indirect effect evolves from their ability to act as cloud condensation nuclei (CCN), influencing cloud droplet number concentration, cloud albedo, precipitation processes and lifetime of clouds (Seinfeld and Pandis 1998) (Charlson, Lovelock et al. 1987) (Andreae, Elbert et al. 1995).

Although present day estimates of the global mean radiative forcing due to anthropogenic aerosol particles are between -0.3 and -3.5 Wm^{-2} (Intergovernmental Panel On Climate 1996) (Seinfeld and Pandis 1998), the aerosol particles responsible for this remain poorly characterized in global climate models (National Research Council (U.S.). Panel on Aerosol Radiative Forcing and Climate Change 1996). The magnitude of the forcing by tropospheric aerosols is poorly constrained, and this represents the single greatest uncertainty in assessing climate change (Intergovernmental Panel On Climate 1996).

As described by the National Research Council (U.S.) Panel on Aerosol Radiative Forcing and Climate Change, accurate quantification of the direct and indirect effect of anthropogenic aerosols on the radiative forcing of climate requires an integrated research program that includes:

- “In-situ measurements covering a globally representative range of natural and anthropogenically perturbed environments to determine the chemical, physical, and radiative properties of the major aerosol types, the relationships among these properties and the processes controlling them,
- Satellite observations to quantify the temporally and spatially varying aerosol distributions, and
- Chemical transport and radiative transfer models to calculate radiative forcing by aerosols and to provide a prognostic analysis of future radiative forcing and climate response under various emission scenarios.”

The Aerosol Characterization Experiments (ACE) are a series of experiments that integrate in-situ measurements, satellite observations, and models to reduce the uncertainty in calculations of the climate forcing due to aerosol particles. The two overall goals of the International Global Atmospheric Chemistry Program Aerosol Characterization Experiments (IGAC-ACE) are:

- Reducing the overall uncertainty in the calculation of climate forcing by aerosols and,
- Understanding the multiphase atmospheric chemical system sufficiently to be able to provide a prognostic analysis of future radiative forcing and climate response.

As indicated in the ACE-Asia Project Prospectus, in order to link global aerosol distributions with the corresponding aerosol optical properties, it is necessary to carry out measurements of aerosol chemical and physical properties, such as the mass distributions of all the chemical species, degree of mixing of various chemical species, and overall size distributions.

C.2.1 ACE-Asia Objectives and Shipboard Measurements

As indicated in the Project Prospectus, the three specific objectives established for ACE-Asia are:

Objective 1. “Determine the physical, chemical, and radiative properties of the major aerosol types in the Eastern Asia and Northwest Pacific region and investigate the relationships among these properties

Objective 2. Quantify the physical and chemical processes controlling the evolution of the major aerosol types and in particular their physical, chemical, and radiative properties.

Objective 3. Develop procedures to extrapolate aerosol properties and processes from local to regional and global scales, and assess the regional direct and indirect radiative forcing by aerosols in the Eastern Asia and Northwest Pacific region.”

As stated in the ACE-Asia Project Prospectus, during the intensive field operations, shipboard measurements will be taken downwind of the Asian continent to contribute to the regional characterization of aerosol properties. These measurements will provide data to test and refine regional chemical transport models. Ship operations will be directed towards sampling regional aerosol features (e.g. dust outbreaks, urban and industrial plumes) under different synoptic meteorological patterns and at different locations and distances from continental influences. The goals of the shipboard studies, as indicated in the Project Prospectus, are to

- a) Determine the physical, chemical and radiative properties of the aerosol in the ACE-Asia region and assess the regional and temporal (diurnal to multi-day) variability of these properties,
- b) Assess the major processes controlling the oxidation mechanisms of aerosol precursor gases and the formation, evolution and deposition of aerosol particles, and
- c) Quantify the direct radiative effect of the combined natural and anthropogenic aerosol in the ACE-Asia study area.

C.3 General objectives for real-time single particle measurements

The main scope of the project proposed herein involves performing real-time measurements of the size and chemical composition of individual aerosol particles using a transportable aerosol-time-of-flight mass spectrometer (ATOFMS) designed at the University of California, Riverside (US Patents 5,681,752 and 5,998,215). The ATOFMS instrument will be operated continuously on board the assigned US Research Vessel from the time it sets sail from Hawaii in March of 2001 until the end of the proposed ACE-Asia intensive field campaign (April 30, 2001).

Over the past decade, a number of research groups developed instrumentation for real-time single particle analysis. A number of different designs were developed (Wood and Prather 1998; Suess and Prather 1999). ATOFMS couples aerodynamic particle sizing with time-of-flight mass spectrometry in a single instrument. This combination allows for measurement of the size and composition of particles in a polydisperse aerosol with high precision, making the information it provides unique from other single particle instruments. Knowledge of precise

particle size is required in order to obtain the transmission efficiency as a function of size for the instrument. This efficiency is determined upon comparison of ATOFMS size distributions with those obtained using co-located sizing instruments (described below). The resulting transmission efficiency allows scaling of the measured ATOFMS size distributions into unique atmospherically representative chemically-resolved size distributions at the single particle level. In addition to revealing distinct size-composition relationships, data at this level clearly shows differences in the degree of external or internal mixing within the aerosol particle population for different particle sizes. ATOFMS is the first single particle technique to provide quantitative data for atmospheric samples over a continuum of particle sizes (Allen, Fergenson et al. 2000).

The principal objectives of this proposal that will help in addressing some of the issues stated for the goals of the ACE-Asia Project (see C.2.1) using ATOFMS include:

- Objective 1** Measure aerosol particle size distributions in the area under study using a transportable ATOFMS and scale the data by comparison with other shipboard particle sizing instrumentation (OPC, SMPS, etc).
- Objective 2** Develop size-resolved aerosol particle chemical composition distributions (including different particle types such as reacted/aged and unreacted sea salt, reacted/aged and unreacted soil and dust, organic-containing particles, elemental carbon and more complex particle types) and compare the results with those obtained with other collocated instruments (e.g. multi-jet cascade impactors) and those present on other platforms.
- Objective 3** Assess the degree of mixing and/or reaction/aging of the aerosol particles measured during the intensive campaign to help: a) evaluate the extent to which observed particles retain their source identity; b) assess the regional and temporal variability of the aerosol particles present, and c) evaluate the ability of the aerosol particles to act as CCN.
- Objective 4** Compare and correlate ATOFMS data with simultaneously acquired optical and radiometric measurements to help quantify the relative impact of chemical speciation within individual particles and the degree of mixing on radiative forcing.
- Objective 5** Compare and correlate ATOFMS data with trajectory data, establishing correlations between particle size and chemical composition with the source of the particles as well as subsequent secondary chemistry processes.
- Objective 6** Carry out necessary laboratory studies in order to reproduce and/or interpret some of the ATOFMS data obtained during the campaign, such as proper mass spectral peak assignment, relative sensitivity measurements for various species (Br^- , BrO_x^- , MSA, HMSA, SO_4^- , etc) and further investigation of the observed heterogeneous reactions. Studies will be performed both before and after the study to test ATOFMS sensitivity towards Br, sulfate, and other species of interest, as well as determine the effect of water content and organic coatings on ion signals.

C.4. Methods

Transportable aerosol time-of-flight mass spectrometer (ATOFMS)

Continuous data on the size and chemical composition of individual particles will be obtained with a transportable aerosol time-of-flight mass spectrometer (ATOFMS) operating on board the designated US Research Vessel.

As described in publications (Prather, Nordmeyer et al. 1994; Noble and Prather 1996), ATOFMS represents a powerful tool that allows for characterization of the aerodynamic diameter and chemical composition of individual particles from a polydisperse aerosol in real-time. The ability to obtain precise size and composition information for all particles in a polydisperse sample is what makes ATOFMS unique from other single particle instruments. Details on the function of the transportable ATOFMS developed at the University of California, Riverside are described elsewhere (Gard, Kleeman et al. 1998).

Briefly, particles are drawn from atmospheric pressure through a converging nozzle into an initial vacuum region held at approximately 3 Torr. Due to the pressure differential, the gas undergoes a supersonic expansion and smaller particles are accelerated to higher terminal velocities than larger particles. After this first stage, the aerosol beam passes through two stages of differential pumping separated by skimmers. The collimated particle beam then enters the light scattering region where the transit time for particles travelling between two scattering lasers is measured and recorded. Upon instrument calibration, as described below, the particle transit time is used to obtain the aerodynamic size of each particle.

Upon exiting the sizing region, the particles immediately enter the ion source region of a dual-ion time-of-flight mass spectrometer. The measured velocity of the particle and known distances between lasers are used for determining when to fire a frequency quadrupled Nd:YAG laser (266 nm) at the exact time the particle arrives in the ion source region, desorbing and ionizing species from each sized particle in flight. Typically, the laser operates at powers between 10^7 and 10^8 Wcm⁻². Both positive and negative ion time-of-flight mass spectra are then correlated with the aerodynamic diameter measured for each particle. It is important to note that ATOFMS provides *both* the positive and negative ion mass spectra for each particle, providing information on all cations and anions present simultaneously (see Figures 1 and 2).

In the first stages of the ATOFMS, particles with smaller aerodynamic diameters diverge more than those with larger aerodynamic diameters. This factor along with others, including detection in the light scattering region and losses in the particle inlet, contribute to differences in transmission efficiency for different particle sizes into the instrument. To correct for these losses, particle number concentration data obtained by PMEL NOAA with a scanning mobility particle sizing system (SMPS; TSI, Inc.) and an optical particle counter (OPC) are used to scale the distributions obtained with the transportable ATOFMS. It is our intention to run an OPC instrument (Particle Measuring Systems, Inc.) alongside the ATOFMS at all times during the entire study.

As mentioned, the ATOFMS instrument used in this study will be calibrated for aerodynamic size in-situ. The corresponding calibration will be carried out using polystyrene latex spheres (PSL, Interfacial Dynamics Corporation) of known aerodynamic diameter. Polystyrene latex spheres (0.1-3.0 μm) will be suspended in water, atomized using a Collison atomizer, dried using two 30-cm diffusion dryers filled with silica gel, and then sent directly into the ATOFMS for size calibration.

Laboratory Studies

As indicated in the objectives (Section C.3), a number of laboratory studies are planned for this project to optimize the ATOFMS for measuring certain species of interest, as well as assist in the interpretation of the data. These studies will be carried out before and after the ACE-Asia Intensive Field Operations. The principal objectives involve the evaluation of necessary relative sensitivity factors for a variety of chemical species of interest, as well as the study of heterogeneous reactions observed during the field campaign. Some of the reactions of interest that will be investigated as part of these studies are those that are expected to affect the chemical composition of sea salt and dust particles during ACE-Asia (and therefore their radiative properties), such as those involving nitric acid (and nitrogen oxides) and sulfur compounds (such as sulfuric acid). The effect of particle water content (i.e. R.H.) on these reactions will also be investigated. Also studies of reactions involving carbon-containing particles will be pursued both of pure organic particles as well as organic coatings on dust and sea salt particle surfaces. The reactions of interest will be carried out in a flow tube reactor and/or environmental chamber. The instrumental setup used for the flow tube experiments allows pre-equilibration of the particles under study to the desired relative humidity values. Different times can be allowed for the reaction of interest to take place by moving the position of the sampling line that carries the particles to the ATOFMS relative to the point where gas and particles are mixed. Also, experiments will be carried out with lower desorption/ionization laser power in the ATOFMS in order to study the chemical composition of the aerosol surface as a function of relative humidity.

Relative sensitivity measurements for various species will also be determined, taking into consideration matrix and relative humidity effects. Knowledge of these factors will allow better evaluation of the data during the ACE-Asia IFO.

C.5 Rationale and Significance

The work proposed here will help in achieving the goals set for ACE-Asia by contributing data on size-resolved single particle chemical composition at a detailed level with high temporal resolution.

ATOFMS single particle studies proposed here will provide insight into the scientific issues addressed in the Science and Implementation Plan for the ACE-Asia Network Studies as described in the following sections.

Regional and Temporal Variability in Aerosol Properties Aerosol Mass Loadings and Composition

As described in the Science and Implementation Plan, the aerosol population in the ACE-Asia region is expected to be a mixture of combustion-derived ionic, inorganic, organic and soot particles, sea salt; mineral dust, biogenic sulfur compounds, trace metals, and a collection of poorly characterized organic species of biogenic origin.

Results from ATOFMS analysis will help determine the detailed composition of the east Asia/Pacific aerosol by providing mass spectral data on single particles. Each particle will produce a mass spectrum with specific ion peaks at certain mass-to-charge (m/z) ratios that can be used to identify the presence of different chemical species. At the single particle level, ATOFMS will provide continuous data on the number of particles containing organic carbon, elemental carbon, soil (reacted/aged and unreacted), sea salt (reacted/aged and unreacted), nitrate, ammonium, sulfate, metals (i.e. V, Fe, Na, Mg, Al, Li, K, Ca, Si, Ti, Ba, Pb, Sn, Ce, and others), and other anions including Cl, Br, and I.

ATOFMS will assist in assessing the degree of mixing of aerosol particles present in the region, since it will allow distinction between internal and external mixtures of particles, as well as identify particles composed of organic species, inorganic species, and combinations. ATOFMS will provide more specific information on the nature of the particles, including indications of organic coatings and degrees of reaction/aging of different particle classes.

Upon being calibrated alongside other instruments, ATOFMS will be used to provide real-time data on the relative percentages of different general particle types detected in the region of interest. The high temporal resolution reported for the ATOFMS will allow determination of changes in aerosol composition across the ACE-Asia region as a function of time of day, location, relative humidity, temperature, etc. Upon comparison with trajectory data, the established correlations will aid in understanding the observed patterns of variation.

Mineral aerosol (Asian dust)

As indicated in the ACE-Asia Science Implementation Plan, it is to be expected that mineral dust will be a dominant component of atmospheric aerosols at various locations and time periods in the region under study. One of the specific issues concerning this type of aerosol has been expressed to be the changes in the chemical composition of dust with time and location across the ACE-Asia domain, information that is currently lacking and essential for quantification of corresponding climatic effects.

ATOFMS single particle analysis will allow the evaluation of changes in chemical composition of particles and will provide information that will be helpful when trying to understand reactions of Asian dust with pollutants and other atmospheric constituents. Both positive and negative ion mass spectra will be obtained for single dust particles which will allow for changes in chemical composition to be evaluated. Positive ion mass spectra will allow for mineral dust particles to be classified according to specific ion combinations in the mass spectra (e.g. Al, Ti, Li, Fe, Ca) and temporal variation of the different classes will be determined. Also, association of dust particles with other constituents (e.g. sulfates, nitrates, organics) can be manifested from the corresponding negative ion mass spectra for the same particle by the presence of particular ion signatures. For example, ion peaks at m/z -62 and -97 indicate the presence of nitrates and sulfates (i.e. NO_3^- , HSO_4^-), respectively. Association of sulfates and nitrates with mineral particles will affect the local cooling effect of the aerosols and will modify the ability of the mineral particles to become CCN (Buseck and Posfai, 1999) (Levin, Ganor et al. 1996; LiJones and Prospero 1998). Also, dominance of mineral dust in aerosol light scattering has been previously reported, showing that mineral dust could be an important climate-forcing agent over regions where dust concentrations are high (Li, Maring et al. 1996).

Also, ATOFMS single particle analysis will assist in quantifying the proportion of anthropogenically generated dust (e.g. industry and transportation) and evaluating the relative contributions to radiative forcing, since different signatures present in the particle mass spectra can be used to distinguish between various classes.

It has been reported that iron in the oceans far from land is provided by continental dust (Duce and Tindale 1991; Martin, Gordon et al. 1991; Martin, Coale et al. 1994). Therefore, iron containing dust particles will affect biological productivity in the North Pacific Ocean (ACE-Asia SIP) (Prospero, Barrett et al. 1996; Prospero 1999). From the mass spectral information obtained with the transportable ATOFMS, it will be possible to classify those particles containing iron and evaluate their contribution to the total aerosol chemical composition, as well as their temporal evolution. These results could then be linked with nutrients and chlorophyll measurements that will be carried out simultaneously by other groups.

Also, ATOFMS single particle analysis will help in characterizing the extent of associations of dust particles with other particle classes, such as sea salt (if they occur during the ACE-Asia IFO). The presence of dust particles associated with sea salt has been previously observed in Beijing (China) and Nagasaki (Japan) (Niimura, Okada et al. 1994; Niimura, Okada et al. 1998), as well as over remote oceans (see for example, Andreae, Charlson et al. 1986).

Carbonaceous aerosol

Ohta and Okita indicate that most of the aerosol mass over East Asia is probably of organic origin, being produced by the abundant combustion sources in the region (Ohta and Okita 1984). Distinction between organic and elemental carbon is essential when trying to estimate radiative forcing due to the opposite effect they can exert. ATOFMS single particle analysis allows some level of distinction between particles containing organic and elemental carbon. Ions commonly observed in the mass spectra of particles classified as carbon containing are those associated with carbon-hydrogen clusters such as $^{12}\text{C}^+$, $^{15}(\text{CH}_3^+)$, $^{24}(\text{C}_2^+)$, $^{27}(\text{C}_2\text{H}_3^+)$, $^{36}(\text{C}_3^+)$, $^{37}(\text{C}_3\text{H}^+)$, and other ion peaks associated with the hydrocarbon envelopes (C_nH_m^+). Some common negative ions found in these particles are $^{12}\text{C}^-$, $^{24}(\text{C}_2^-)$, $^{25}(\text{C}_2\text{H}^-)$, $^{36}(\text{C}_3^-)$, and $^{48}(\text{C}_4^-)$. In the case of particles classified as elemental carbon, it is possible to observe in the positive ion mass spectra the presence of carbon ion clusters that extend to higher m/z than for the case of carbon containing particles. Usually the intensity of the singly protonated clusters (C_nH^+) present in the spectra are much lower than in the case of carbon containing particles, and higher protonated clusters are usually missing in this particle class. In the negative ion mass spectra, a peak at m/z -72 (C_6^-) is usually observed.

It is also common to find, in the positive-ion mass spectra of carbon containing particles, a peak due to $^{39}\text{K}^+$, which is an indicator of combustion sources such as biomass burning and meat cooking. Information contained in the negative ion mass spectra of these particles allows further distinction between these two different sources. The importance of biomass burning in aerosol forcing has also been described previously (Crutzen and Andreae 1990; Penner, Dickinson et al. 1992). Association of carbon containing particles with other species is evident in ATOFMS spectra, where the presence of particular ion signatures can be evaluated. For example, a peak at m/z -97 will commonly be observed in the negative ion mass spectra of carbon containing particles. The presence of this peak, which can be assigned to $^{97}\text{HSO}_4^-$, indicates the presence of sulfate in the particle. The presence of soot/sulfate aggregates has been observed not only in polluted urban environments (Buseck and Posfai, 1999) (Okada 1985; Parungo, Nagamoto et al. 1994), but also in remote oceanic atmosphere (e.g. during ACE-1 and INDOEX) (Buseck and Posfai, 1999). When sulfate is associated with a particle of elemental carbon characteristics, both the absorption properties of elemental carbon and the scattering effect of sulfates have to be considered to evaluate the overall radiative properties of that particular type of particle (e.g. (FassiFihri, Suhre et al. 1997)). Also, the hygroscopic properties of particles of this chemical composition will be determined by the presence of insoluble matter (elemental carbon) and hydrophilic matter (sulfates), therefore affecting the ultimate potential for these particles to be activated into cloud condensation nuclei (and hence the droplet formation).

Major Ions

Sulfate and nitrate are considered to be major components of the aerosols present in the ACE-Asia region (ACE-Asia SIP) and further assessments of their sources are proposed for this

project. The relevance of these ions arises from the fact that they are involved in a variety of chemical reactions that modify the characteristics of the aerosol present in the region, and the importance they have on radiative forcing (e.g. (Kiehl and Briegleb 1993; Langmann, Herzog et al. 1998; Kirkevåg, Iversen et al. 1999)).

For example, determination of the associations of sulfate with other particle classes is very important when radiative properties are considered, because it will be the combination of different constituents in a particle what will ultimately determine the scattering and absorption properties of that particle. Also, the association of sulfates with other particle classes will affect the hygroscopic behavior of the particle and will determine its fate as a CCN.

Sulfates can be associated with different particle classes such as sea-salt, dust, elemental carbon, organic matter, etc. (Levin, Ganor et al. 1996; Clegg and Toumi 1998; LiJones and Prospero 1998; Murphy, Anderson et al. 1998; Posfai, Anderson et al. 1999) (Sievering, Boatman et al. 1991; Suhre, Andreae et al. 1995; Huebert, Zhuang et al. 1996; Odowd, Smith et al. 1997; Clegg and Toumi 1998). ATOFMS single particle analysis will help to evaluate the relative proportions of these sulfate-associated particle types, which will be essential for evaluating the direct and indirect effect of sulfate aerosols in the region under consideration.

The presence of non sea salt (nss) sulfate on sea salt particles is evidenced in ATOFMS single particle analysis by the presence of a peak in the mass spectra at m/z 165 Da that can be assigned to $(\text{Na}_3\text{SO}_4^+)$ (see Figure 1). In this type of particle, the sulfate could be the result of sulfate uptake by condensation of sulfuric acid (or organic sulfates) from the gas phase and/or by conversion of dissolved SO_2 (Clegg and Toumi 1998; Kerminen, Teinila et al. 1998) (McInnes, Covert et al. 1994; Song and Carmichael 1999). Also, in organic particles, the presence of ion peaks at m/z -80, -96, and -97 can indicate the presence of sulfite, sulfate, and bisulfate, respectively. Preliminary results also show that ATOFMS single particle analysis may help in identifying the presence of MSA and/or HMSA in sea salt particles. In the case of MSA, a peak at mass-to charge ratio -95 Da is observed in the negative mass spectrum (assigned to $^{95}(\text{CH}_3\text{SO}_3^-)$) and a peak at m/z 141 (assigned to $^{141}(\text{Na}_2\text{CH}_3\text{SO}_3^+)$) is observed in the positive ion mass spectrum of the corresponding sea salt particle. In the case of HMSA, a peak at m/z -111 Da that can be assigned to $^{111}(\text{HOCH}_2\text{SO}_3^-)$ is observed in the corresponding negative ion mass spectrum of certain particles containing organics. Also, ATOFMS can identify the presence of nitrates on different particles. For example, the presence of nitrates on sea salt particles, with the consequent chlorine displacement and formation of sodium nitrate in the particle phase, can be indicated by the presence of $^{108}(\text{Na}_2\text{NO}_3^+)$ in the positive ion mass spectra of these particles (Gard, Kleeman et al. 1998). Also, peaks at m/z 30, -46, and -62 (assigned to NO^+ , NO_2^- , NO_3^-) can indicate the presence of nitrates in single particles.

The presence of organics on particles of inorganic characteristics can also be determined by ATOFMS analysis. For example, sea salt particles with organic matter will contain additional mass spectral peaks due to $^{12}\text{C}^+$ and $^{12}\text{C}^-$. The presence of organic matter in these particles could be the result of heterogeneous reactions and/or condensation of organic vapors (Kerminen, Teinila et al. 1998). As described previously, the association of sulfates with carbon containing particles can be determined by ATOFMS analysis as well. These kinds of associations are relevant when determining climate effects, since they will influence the hygroscopic behavior of the particles (Andrews and Larson 1993, Saxena, Hildemann et al. 1995).

Correlations between different aerosol species can be established from ATOFMS analysis, allowing the study of differences in air masses and the characteristics of the continental outflow in the region.

Other aerosol components and chemical tracers

Information on aerosol sources, such as biomass burning, can be inferred by the presence of certain trace metals. Some of the trace elements that can be detected with ATOFMS include: K, Be, V, Fe, Mg, Al, Li, Ca, Si, Ti, Ba, Pb, Sn, Ce, Mn. The presence of these elements in different particle classes, alone or combined, will provide information on the possible sources of such detected particles.

As reported by Hashimoto et al. in 1994, levels of certain toxic metals, such as lead from gasoline, are expected to be high in the ACE-Asia region. The isotopic combinations of peaks for various metals confirm the assignment of the corresponding ion peaks. For example, the presence of lead in single particles is indicated by the presence of isotopic peaks at m/z 204, 206, 207 and 208 in the positive ion mass spectra.

C.6. Statistical Analysis

The ATOFMS instrument will continuously sample individual aerosol particles 24 hours a day for the duration of the study. For each particle, information on the particle speed (related with the particle aerodynamic diameter) and both positive and negative ions mass spectra will be stored. Depending on atmospheric particle concentrations, ATOFMS will acquire the specified information for 800-1500 particles per hour. The temporal resolution for the reported chemical species and particle classes will depend on the current particle concentrations. At typical urban particle concentrations, ATOFMS provides data on desired species with 10-minute resolution (Liu, Hering et al. 1999).

All data acquired during the proposed study will be stored in an Access database to allow for rapid data processing on-site and after the study is completed. This database will allow searches on any chemical species or particle classes for the entire time period of the study. Since we expect to detect an average of approximately 1000 particles per hour, the corresponding stored information (e.g. 2000 spectra per hour) will provide an extensive data set that will allow statistical evaluation by accepted methods.

Also an adaptive neural network program, ART-2A, can be used to rapidly classify the detected particles. ART-2a is a method for automatically classifying particles with similar spectra without the need for human intervention or prior knowledge of the nature of the particles in a particular area. The advantage ART-2A presents is that it can be used as the data are being acquired to measure concentrations of previously detected particle types while presenting information on any newly detected particle types (Song, Hopke et al. 1999).

As mentioned previously, to obtain atmospherically relevant particle number concentrations, ATOFMS single particle data are scaled to account for transmission efficiency. This scaling process results from the comparison of ATOFMS data with data acquired by other more conventional particle sampling instruments, including an optical particle counter (OPC), scanning mobility particle sizing system (SMPS), and MOUDI impactors. Results from previously performed comparisons showed the validity and utility of this procedure (Hughes, Allen et al. 1999; Allen, Fergenson et al. 2000).